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Furan Functionalized Polyesters and Polyurethanes for Thermally Reversible Reactive Hotmelt Adhesives

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Abstract

New reactive hotmelt (RHM) adhesives based on thermally reversible Diels-Alder networks comprising multifunctional furan and maleimide prepolymers are described. The prepolymer mixture is easy to apply in the bulk from the melt and after application to the substrates, the adhesive undergoes polymerization at room temperature resulting in crosslinked bonds. Due to their thermoplastic nature and low melt viscosity at hot melt application temperatures, the adhesives provide processing properties similar to moisture cured polyurethanes (PUR). The technology is isocyanate-free and does not require moisture to initiate the crosslinking. Bonding and tensile properties of the RHM adhesive can be readily tuned by prepolymer design and provide cure rates similar to PUR adhesives. The Diels-Alder adhesives provide versatile adhesion to a variety of substrates and good creep resistance up to the retro temperature. The adhesives show good thermal stability during application and can be recycled multiple times by simple heating/cooling of the bonds providing similar performance. Several furan and maleimide prepolymers were scaled up to multi-Kg quantities to demonstrate the potential for industrial scalability. The results demonstrate that furan-maleimide reversible chemistry can be used for RHM application as a more sustainable alternative to conventional moisture curing PURs which tend to contain harmful residual isocyanate monomers.

Keywords: Furan, maleimide, polyurethane, thermally reversible, recyclable, moisture-free, isocyanate-free, de-bonding

1. Introduction

Several furan derivatives such as furfuryl alcohol, furfural and 5-hydroxymethylfurfural are bioderived. The industrial use of furan derivatives in polymeric applications is increasing - for example, furfuryl alcohol and furfural are used as raw materials to make furan resin, which is applied as a binder in polymeric concrete for construction [1]. 5-Hydroxymethylfurfural is a bioderived precursor for making 2,5-furandicarboxylic acid, which is a raw material used to make polyesters that are projected to replace phthalate plasticizers and even PET [2]. Other polymeric applications of furan derivatives include copolymerization in phenol-formaldehyde system [3], melamine-formaldehyde [4] and in biomedical applications [5]. In

addition, benzofuran type highly conjugated furan functional polyaromatics have been used in organic solar cells [6]. On an industrial scale, Furnova Polymers Ltd. sells several furan based polymeric materials for concrete, anticorrosion, composites and high temperature applications. Another potential application of furan derivatives is reversible crosslinking to generate polymers that can be used to bond substrates and which can be reworked or de-bonded by depolymerization at high temperatures caused by the retro Diels-Alder reaction. Incorporation of furan-maleimide based thermally reversible covalent crosslinks into polymers is known [7]. Upon heating above 80°C, the crosslinks dissociate and upon cooling the crosslinks reform. This property has been used in a number of applications such as in interpenetrating networks [8], remendability [9] and self-healing [10]. Adhesives are widely used to bond substrates in a number of consumer and industrial applications [11]. Crosslinked adhesives provide the highest bond strength and durability but have a negative environmental impact, since permanent adhesion prevents easy separation at their end-of-life which does not facilitate the re-use or recycling of materials. With increasingly stringent requirements for meeting fuel economy and recycling targets, the automotive and electronic industry has a strong need for debondable/reworkable adhesives that enable efficient repositioning in defective assemblies or end-of-life cycle recycling. Adhesives have also been used to replace metal fasteners to make the assembly lighter and thus help meet the fuel economy target. There have been several reports on the use of maleimide-furan Diels-Alder networks for reversible adhesives that include epoxy [12], polyacrylates [13] and polyurethanes [14]. However, in these reports, a low molecular weight monomeric maleimide compound such as *N,N'*-(4,4'-methylene diphenyl) bismaleimide (BMI), which is readily available commercially, was used. However, this BMI is highly toxic and unsuitable for practical consumer or industrial adhesive applications. It also has poor compatibility with most resin systems because of its rigid aromatic backbone and high polarity. While Diels-Alder based reversible non-isocyanate polyurethanes have been described before [14], little is known on their material properties. Most of the reported reversible polymeric systems based on furan-maleimide Diels-Alder networks required exposure to hot solvents for effective removal of components. In summary, the incorporation of Diels-Alder chemistry in a truly practical fashion has not yet been demonstrated.

Traditional hot melt adhesives based on, for example, polyolefins or polyamides are thermoplastic polymers which melt upon heating so that they can be applied to a substrate in a fluid state when hot. The cohesive strength of these adhesives is derived primarily from intermolecular physical forces which are formed upon cooling the adhesive. Polyurethane RHM adhesives are also applied in molten form and initial (green) strength is provided on cooling into a solid state. However, these adhesives are reactive (made from isocyanate functional prepolymers) which cure by moisture over time at ambient temperature resulting in adhesives with improved performance, such as adhesion strength, heat resistance, toughness and chemical resistance [15] when compared to thermoplastic hotmelts. The isocyanate prepolymers are typically made by reacting excess diisocyanates such as 4,4'-methylenedi-phenyl diisocyanate (MDI) with polyols. Practical use of this chemistry (lower viscosity at hotmelt application temperature) requires that a NCO/OH ratio in the range 1.5 to 2.3 should be used for the synthesis of isocyanate prepolymers. The resulting compositions usually contain residual diisocyanates such as MDI, which are respiratory and skin sensitizers. Despite the successful development of moisture curable RHM, the technology has some limitations. For example, RHMs must be stored in the absence of moisture to prevent premature curing and require specialized application equipment for processing to keep moisture out. The cure rates of RHM's can also vary depending on atmospheric humidity level, moisture content

of the substrates, bond line thickness and moisture vapor transmission rate of the adhesive [16]. The compositions cure irreversibly and such adhesives cannot be used in applications where features such as repositionability, reworkability or recyclability are desired. There remains a need for improvement in RHM technology. Here we report on a new thermally reversible RHM that undergoes cross-linking at room temperature after application from the melt by copolymerization of polyfunctional furans and maleimides. Poly(ester urethane)-based prepolymers with maleimide end groups are developed and combined with the polyfunctional furans to provide thermally reversible polyurethane RHM's that are isocyanate-free and exhibit a range of physical properties similar to conventional polyurethane based RHMs. The new adhesives can be bonded, de-bonded and re-bonded multiple times without a significant change in performance.

2. Results and discussion

2.1 Initial proof-of-concept, ambient curing and cured adhesive strength

The thermally reversible RHM concept is schematically represented in **Figure 1** involving the dynamic equilibrium of Diels-Alder networks based on the combination of a polyfunctional furan crosslinker (indicated in blue color) and a maleimide prepolymer (indicated in red color). In the hotmelt state at higher temperatures (left hand side), network dissociation is favored - the Diels-Alder equilibrium is shifted toward free furan and maleimide functional prepolymers that provides the molten state. The fluid adhesive is then applied to substrates and after cooling, the prepolymers form crosslinked adhesive at ambient temperature via the $[4 + 2]$ cycloaddition reaction between furan and maleimide functional groups (right hand side).

Reactive PUR hot melts are desirable due to their ease of application (involving low melt viscosity), high initial green (uncured) strength, curing at ambient temperature and versatile cured adhesion/durability. For initial investigations into the suitability of this concept, a variety of polyfunctional furans and maleimides were made in order to critically determine if they could behave like PUR hotmelts currently in use, i.e. (a) be applied as a fluid hotmelt at moderate temperatures, (b) crosslink at ambient temperature over a reasonable time period and (c) provide

Figure 1. Thermally reversible reactive hotmelt concept. For clarity, furan and maleimide functional reacting prepolymers are indicated in blue and red colors, respectively (see text for description).

suitable cured bond strengths. To this end, a number of polyfunctional furans and maleimides were made, formulated into reactive hot melts and compared to a reference commercially available PUR adhesive. Polyfunctional furans F-1, F-2, F-3, F-4, F-5 & F-6 comprising ester and urethane linkages were made (**Figure 2**). F-2, F-3, F-4 and F-5 were made by simple addition of bio renewable furfuryl alcohol to the corresponding commercially available isocyanates. To mimic polyurethane like properties, F-6 possessing a PU backbone was made by initially reacting polyester or polyether polyols with MDI followed by bulk addition of furfuryl alcohol in the same pot. Trifunctional furan F-1 was synthesized by reacting 1,3,5-benzenetri-carbonyl chloride with furfuryl alcohol in the presence of triethylamine as base in a solvent [17]. When the isocyanate starting material are liquids, a bulk process can be used to make the corresponding polyfunctional furans. For example, F-2, F-5 and F-6 were made in the bulk without the use of solvents simply by slow addition of furfuryl alcohol to the corresponding isocyanates. The polyfunctional isocyanate starting material used for F-3 synthesis is commercially supplied in 25% butyl acetate solvent and it was used as supplied. Several batches of polyfunctional furans were made at multi-Kg scale to demonstrate the industrial scalability of the process [18].

Figure 2.
Polyfunctional furan resins used in the study.

Figure 3.
Bismaleimide (BMI) resins used in the investigation.

Several bismaleimide resins (BMI) were also investigated as components in the study (**Figure 3**). M-1 is a liquid BMI supplied by Henkel Corporation and it has a flexible 36-carbon dimer diol backbone (represented as C₃₆). Two maleimide prepolymers M-2 & M-3, possessing poly(ester urethane) backbones were also used (discussed in detail in the later part of this chapter). Both the resins M-2 and M-3 were made in a bulk process by first reacting corresponding polyester polyols with excess MDI and subsequently capping the isocyanate terminated polyurethane prepolymers with 2-hydroxyethylmaleimide in a 2-step, one-pot process similar to the process used for the synthesis of F-6 [18]. The polyester polyols used for M-2 and M-3 (Dynacoll 7360 and 7231, respectively - obtained from Evonik) are used in typical moisture cured RHM formulations. Since excess diisocyanate is used in step 1 (1:2 stoichiometry of diol to diisocyanate used, some chain extension observed), a minor reaction product arising from the reaction of residual MDI remaining from step 1 with 2-hydroxyethylmaleimide was also observed. However, these adducts are nonvolatile as a consequence of their higher molecular weight and polarity (urethane & maleimide functionalities) as compared to MDI itself. Due to the presence of polyfunctional furans in the melt, they will be incorporated into the crosslinked Diels-Alder network. This is in stark contrast to conventional moisture cured RHM's based on isocyanate prepolymers, where the toxicity arises primarily from the volatility of residual MDI (at hotmelt application temperature) and potential hydrolysis to the corresponding aromatic amine. Prepolymers M-2 & M-3 possess semicrystalline and amorphous polyester backbones, respectively, and were used to investigate their impact on properties. A commercially available rigid aromatic bismaleimide M-4 (Daiwakasei industry) was also investigated as an additive in formulations to study its effect on properties. Several other polyfunctional maleimides were also made by simple addition of 2-hydroxyethylmaleimide to polyfunctional isocyanates by a process similar to that used for the synthesis of polyfunctional furans described in **Figure 2**. However, initial formulation work by blending these polyfunctional maleimides with furan prepolymers F-6 (possessing PU backbone) did not show much promise likely as a result of compatibility issues between highly polar polyfunctional maleimides and F-6. Hence, this approach was not pursued further.

Our initial formulation work focused on the feasibility of achieving room temperature cure and identifying structural features that contributed to bond strength at room temperature and 80°C. The components of formulas DA-1 to DA-7 shown in **Table 1** were mixed in the melt (typically at 120–150°C) until they became

Formula	F-1	F-2	F-3	F-4	F-5	M-1	M-2	M-3	M-4	Lap shear ^a	Lap shear ^b
DA-1	24.4					75.6				5.4	0.8
DA-2		36.8				63.2				5.8	0.7
DA-3			49.2			50.8				2.0	1.8
DA-4			17.5				25	57.5		5.0	0.9
DA-5				32		68				3.1	1.5
DA-6	27					63			10	3.3	1.8
DA-7	14				25	51			10	5.6	0.7
DA-8					44	56				n.d.	n.d.
Control ^c (PUR)										4.9	1.1

^aLap shear strength tested at ambient temperature [beechwood substrate, 25 × 25 mm bond overlap], unit MPa.

^bLap shear strength tested at 80°C in air circulated oven [beechwood substrate, 25 × 25 mm bond overlap], unit MPa.

^cA commercial isocyanate prepolymer from Henkel corporation was used as a reference.

n.d. means not determined.

The lap shear samples were tested using a JJ Lloyd tensiometer, with a load cell of 10 kN & a crosshead speed of 100 mm.min⁻¹.

Table 1.
Diels-Alder formulations investigated in the study. The formulation components shown are in weight % (wt%).

completely homogenous followed by coating on Beechwood substrate (250 µm coating thickness, see **Table 1**) and subsequent bonding.

The bonded substrates were allowed to cure at 23°C for 1 week at 50% relative humidity (RH) before testing for lap shear strength. As a control, a commercial isocyanate terminated polyurethane prepolymer (PUR) from Henkel Corporation was used. This control was bonded, cured at room temperature for 1 week and tested in the same way as the Diels-Alder based formulations.

Formula DA-1, which used a flexible BMI resin M-1 showed good curability at room temperature as evidenced by good lap shear strength development (DA-1 v PUR). Owing to the inherent thermal reversibility of the network, the lap shear strength at 80°C was slightly inferior to the control PUR. The addition of 10 wt% of rigid aromatic BMI M-4 improved the hot strength at 80°C (DA-6 vs. DA-1). However, the room temperature curability of DA-6 was negatively affected as evidenced by the lower lap shear strength. This is likely a result of a higher glass transition temperature (T_g) of the network which would restrict mobility of the reactants at room temperature. By partially substituting F-1 with flexible bifunctional F-5 (maintaining crosslinks in the network), the room temperature curability was improved at the expense of 80°C strength (DA-7 v DA-6). Similar observations were made with formulas DA-2 and DA-3. Use of flexible furan F-2 in DA-2 gave good lap shear strength at room temperature. In contrast, rigid furan F-3 used in formula DA-3 improved the hot lap shear strength at the expense of room temperature strength. Formula DA-5 that contains F-4 with a rigid aromatic backbone showed lap shear performance similar to DA-3 at both room temperature and 80°C. For comparison, a linear Diels-Alder network (DA-8 formula) was made by blending bifunctional precursors F-5 and M-1 and allowing to copolymerize at room temperature for 3 days. A size exclusion chromatography (SEC) molecular weight comparison of this polymer with M-1 and F-5 showed a several-fold increase in molecular weight arising from step-growth polymerization at room temperature (**Figure 4**). In addition, there were very low levels of reactants M-1 & F-5 present. While both M-1 and F-5 are medium viscosity liquids at ambient temperature (2,000–5,000 cP), the linear polymer was a gel like material at room temperature

Figure 4. SEC chromatogram comparison for M-1 ($M_p = 1298$ Da), F-5 ($M_p = 1116$ Da) and the corresponding linear Diels-Alder polymer DA-8 ($M_p = 15294$ Da). Mp refers to peak molecular weight. The chromatograms were run using Waters e2695 instrument comprising three Agilent Polypore 7.8 $\times$ 300 mm GPC columns using THF as mobile phase and Waters 2414 as a RI detector against polystyrene standards.

and a liquid at 60°C as a likely consequence of low T_g (both M-1 and F-5 possess flexible backbones). No lap shear measurements were performed on this system. The molecular weight for the polymer is likely to increase further if left at room temperature for a longer time period since it would take about a week for high prepolymer conversion (discussed later in the chapter). The SEC data presented here further demonstrates the room temperature reactivity of the Diels-Alder based systems.

The cause of contrasting lap shear results obtained with formulations DA-2 and DA-3, which contain the same maleimide component M-1 but structurally different furans F-2 and F-3, respectively, was investigated by differential scanning calorimetry (DSC) studies. It should be noted that F-2 contains a flexible backbone while F-3 possesses a highly rigid cycloaliphatic backbone. **Figure 5** shows DSC thermograms for neat F-2 and F-3, and the corresponding formulas DA-2 and DA-3, respectively. Polyfunctional furan F-2 appears to be completely compatible in the DA-2 formulation with only a T_g at 10°C for the crosslinked network and

Figure 5. DSC thermograms (TA instruments Discovery DSC 25) of F-2, DA-2, F-3 and DA-3. Reproduced from [17] with permission from Royal Society of Chemistry.

an endotherm above 100°C corresponding to the retro Diels-Alder depolymerization. No residual melting point for F-2 was recorded. In contrast, the cured DA-3 network shows a residual melting point at 76.7° C for F-3 along with the expected endotherm for the depolymerization. This indicates that the rigid F-3 is partially incompatible at room temperature in DA-3, which could explain the lower lap shear strength obtained at room temperature (DA-3, **Table 1**). The partial incompatibility could also be resulting from the higher concentration of F-3 (higher molecular weight) required in DA-3 (as compared to DA-2) for 1:1 molar equivalence between furan and maleimide functionalities. The higher T_g of the partially cured network is also likely contributing to incomplete polymerization at room temperature. The DA-3 formula likely needs to be heated to above the melting point of F-3 for better compatibility, which is reflected in higher lap shear strength observed at 80°C. A similar effect may be operating in DA-5, which uses rigid furan F-4, although this was not investigated in detail.

Since the Diels-Alder network formation does not require moisture for curing, in principle the cure rate is independent of moisture availability. **Figure 6** shows comparison of cured films of DA-1 and the moisture cured PUR control. The DA-1 cured film appears clean without bubbles (**Figure 6**, left image). In contrast, the moisture curing PUR control shows significant bubble generation arising from CO₂ evolution during moisture cure (right image). If CO₂ cannot diffuse out of the bond line during application, the pressure generated can cause substrate deformation, especially when non-porous substrates are bonded together, such as plastics and metals.

Overall, these preliminary results indicate that a combination of both soft and rigid backbones are required in the prepolymers to obtain a balance of adhesion strength at room temperature and 80°C. The effect of T_g of the crosslinked network on prepolymer conversion at room temperature is discussed in detail at a later section. Formula DA-4, which used the rigid F-3 crosslinker and two bismaleimides M-2 and M-3 possessing poly(ester urethane) backbones showed lap shear performance very similar to the PUR control. This initial investigation showed that the new thermally reversible RHM could be applied as fluid hotmelts at moderate temperatures, would cure at similar rates to conventional PUR at ambient temperature and that similar bond strengths could be achieved. Based on these initial results, DA-1 and DA-4 were selected for more detailed investigations.

Figure 6.
Appearance of cured films of DA-1 (left) and moisture cured PUR control (right).

Figure 7.
Melt viscosity of DA-4 at different application temperatures as a function of time (run using Brookfield Viscometer model RVDV-1 with a Model 74R temperature controller and Thermosel unit using spindle no. 27). Reproduced from [17] with permission from Royal Society of Chemistry.

2.2 Thermal stability

In real world applications, RHM adhesives are held at the desired application temperature (e.g. in the range 120–150°C) for a number of hours until all the substrates are coated and bonded in the production line. This requires good thermal stability up to several hours in the open air. To investigate the stability of the Diels-Alder RHM system, DA-4 (which is compositionally closest to PUR) was held at a specified melt temperature and the viscosity was measured as a function of time using a Brookfield viscometer (**Figure 7**). The initial melt viscosity is in the range 7,000–17,000 mPa.s at 135°C and 150°C, similar to the melt viscosity of PUR products which provide good substrate wetting. The DA-4 formula also shows good thermal stability at 135°C and 150°C up to about 6 hours. It should be noted that the viscosity profile of the DA-4 at these temperatures is very similar to the moisture cure PUR benchmark. To test the limit of thermal stability, DA-4 was also held at 180°C for several hours. However, significant viscosity increase was observed likely arising from homopolymerization of the free maleimide component. It should be noted that this is not a typical temperature used for reactive hotmelts in current industrial applications since the NCO prepolymers would be highly unstable at these temperatures as trimerization of isocyanate functionality is possible.

2.3 Green (initial) strength

An important processing property requirement of RHM adhesives is green strength, which is the initial bond strength soon after the adhesive is applied from the melt and before moisture curing takes place. Liquid NCO prepolymers applied at ambient temperature have very little green strength as there is little cohesion to keep substrates apart, and substrates need to be clamped together before sufficient strength is built up. However, reactive PUR hot melts have the advantage that the green strength is relatively high and additional steps are not required to hold substrates together before curing takes place. This results from non-covalent interactions providing physical strength on cooling, provided by hydrogen bonding and crystallization. DA-1 and DA-6 (similar formulas but DA-6 with 10% additive) were

Figure 8.

Green strength development comparison of DA-1 (red), DA-6 (green) with PUR control (blue). Test performed on ARES-M rheometer (TA instruments) using dynamic oscillatory test method in which 10 rad/s oscillating frequency was used with 1% strain and the data recorded at 11 second intervals.

evaluated for green strength in comparison to the PUR reference by rheological analysis. Experiments were performed with rapid cooling where adhesive compositions were positioned between parallel plates cooled from application temperature to 40°C at a cooling rate of 60°C per minute in nitrogen atmosphere, and then held for 20 minutes to evaluate the storage modulus (elastic component) as a function of time. **Figure 8** shows that DA-1 (comprising a very flexible aliphatic backbone) has a lower modulus than the PUR reference. However, this can be tuned since DA-6 (similar to DA-1 but with 10% additive) provides higher green strength than the reference as a consequence of the incorporation of a rigid, aromatic backbone. These results indicate that the green strength of Diels-Alder based RHM systems can be tuned by the appropriate choice of prepolymer composition.

2.4 Cure dynamics and adhesion development

FT IR spectroscopy was used to investigate the ambient temperature conversion of the DA-1 composition after deposition from the melt by monitoring the characteristic maleimide absorption at 696 cm^{-1} (**Figure 9**). In the cured film (top IR trace indicated in black color), the 696 cm^{-1} band is not visible. After heating the film at 150°C for 1 h and immediately cooling, this band is prominent initially but decreases in intensity as the crosslinking progresses. The decrease is rapid in the first two days after deposition followed by a slower change in the next several days. The band is barely visible after 10 days of storage at room temperature.

In a separate experiment, the composition DA-1 was applied from the bulk between two Beechwood substrates (25 × 25 mm bond overlap) and bond strength development was compared over time at room temperature and at 60°C (**Figure 10**). At room temperature, the bond strength increases substantially over a period of 48 hours before tending to a plateau. This is consistent with the decrease of the maleimide absorption peak at 696 cm^{-1} as Diels-Alder cycloaddition progresses as shown in **Figure 9**. It is interesting to note that substrate failure begins to occur at a bond strength of about 4 MPa and that this is reached in approximately 24 hours at room temperature. In comparison, the strength development at 60°C is more rapid and reaches 4 MPa in approximately 2 hours.

Figure 9.
IR spectra of DA-1 cured network over the range 600–1000 cm^{-1} before heating (top) and over time at ambient temperature after deposition from the melt. IR measurements were recorded using a PerkinElmer FT-Infra-red spectrometer equipped with a UATR Two accessory. Reproduced from [17] with permission from Royal Society of Chemistry.

Figure 10.
Comparison of lap shear strength development on Beechwood substrate for DA-1 formulation at room temperature (RT) and 60°C as a function of time.

2.5 Cured properties and adhesion

For isocyanate terminated PUR moisture cure adhesives, the mechanical performance is determined by a combination of covalent crosslinking formed by moisture curing (including urea formation), H-bonding of urethane groups and crystallinity from polyester segments present in the prepolymer backbone. The urethane and urea groups contribute to the flexibility & elongation of the cured network while the crystallinity of the polyester segment causes further reinforcement of modulus and stiffness. The results discussed previously demonstrated that the lap shear strength, room temperature curability and mechanical properties can be tuned by proper choice of polyfunctional furans possessing rigid or flexible backbones. However, to achieve properties similar to moisture cured PUR, the use of polyurethane backbones with reinforcing crystalline segments is necessary. We sought to achieve this initially by making furan functional PU prepolymers F-6 possessing semicrystalline polyester segments and blending them with polyfunctional maleimides obtained by the addition of 2-hydroxyethylmaleimide with polyfunctional isocyanates. However, our initial results did not show promise likely as a

result of compatibility issues. As an alternative approach, maleimide terminated PU prepolymers M-2 & M-3 possessing poly(ester urethane) backbones were made (**Figure 3**) in a one-pot bulk process and formulated with polyfunctional furans. The synthetic process is very similar to that utilized for the synthesis of isocyanate terminated PUR prepolymers except that an additional solvent-free process was used to react the terminal isocyanate groups with 2-hydroxyethylmaleimide in the same-pot [18]. The prepolymers were scaled up to several Kgs with reproducible performance (discussed in the next section) to demonstrate the industrial scalability of the process. A blend of M-2 comprising a semi-crystalline backbone and M-3 with amorphous polyester segment was used to achieve a balance of room temperature and 80°C lap shear strength. Such combinations of semi-crystalline and amorphous polyester polyol segments are also used in moisture cured PUR products to provide the necessary balance of properties suitable for applications.

The DSC thermogram for the cured DA-4 network shows a T_g of -11.7°C and a melting point (T_m) at 50.8°C for the semi-crystalline polyester segment present in copolymerized prepolymer M-2 (also seen in the DSC thermogram of M-2). In addition, there is an endotherm at 140.4°C resulting from the retro Diels-Alder depolymerization (**Figure 11**). We have previously shown that the position of this endotherm is a function of the heating rate, with much lower temperatures obtained at 1°C per minute compared to 10°C per minute [17]. Compared to DA-4, the thermograms for DA-2 and DA-1 do not exhibit a melting point due to the amorphous backbones but have higher T_g values of 10.0°C and 47.3°C , respectively. In addition, the peak position and magnitude of the endotherms due to the retro Diels-Alder reactions are relatively low for DA-4 compared to the DA-1 and DA-2. This is due to the relatively lower crosslink density in DA-4 arising from lower concentration of furan and maleimide functional groups since the molecular weights of M-2 and M-3 are much higher compared to M-1 used in DA-1 and DA-2. A similar phenomenon has been observed in self-healing coatings [19]. It is important to note that no residual melting point for F-3 was seen in DA-4, which indicates good compatibility in the formula (compared to DA-3, **Figure 5**).

The conversion in the Diels-Alder polymerization of DA-1, DA-2 and DA-4 formulas was investigated after deposition from the melt by monitoring the characteristic absorption at 696 cm^{-1} for the maleimide functionality. **Figure 12** shows the relative intensities of this band as a function of time. The initial absorption

Figure 11.

DSC thermogram for DA-4 and comparison with M-2, DA-1 and DA-2 (TA instruments Discovery DSC 25). Reproduced from [17] with permission from Royal Society of Chemistry.

Figure 12.

IR absorbance comparison of maleimide absorption at 696 cm^{-1} as a function of time for DA-1, DA-2 and DA-4. Absorbance values after 7 days are: 0.027 for DA-1 (82% conversion), 0.014 for DA-2 (88% conversion) and 0.003 for DA-4 (95% conversion). Reproduced from [17] with permission from Royal Society of Chemistry.

intensities correspond well to the relative concentration of the maleimide functionality in the 3 formulas ($\text{DA-1} > \text{DA-2} > \text{DA-4}$). In spite of the significant difference in reactive functional group density, prepolymer molecular weight and backbone, all the three formulas showed a similar reactivity tendency in the first 48 hours. There was fast reduction in the first 48 hours, followed by slower decrease, before reaching a plateau at 7 days. A closer look at the relative absorption after 7 days however showed some difference in conversion. DA-4 with the lowest T_g (-11.7°C) shows the highest conversion (95%) while DA-1 with the highest T_g shows the lowest conversion (82%). This result is consistent with higher mobility typically seen in lower T_g networks. The lower room temperature lap shear strength previously observed with compositions DA-3, DA-5 and DA-6, which used polyfunctional furans with rigid backbones, are also likely to result from lower conversion due to restricted mobility (**Table 1**). These formulas showed better 80°C lap shear strength than the PUR reference.

The bond strengths of DA-1 & DA-4 were compared to the control PUR system on three different types of material substrates – wood, plastic and metal (**Figure 13**). For bonding Beechwood substrates at ambient temperature, the lap shear strengths of both Diels-Alder networks were similar to the reference PUR. However, at 80°C the bonding performance was slightly better for the irreversible PUR system (**Figure 13A**). The bond strength of DA-4 on polycarbonate (PC) was slightly superior to the reference PUR at ambient temperature (**Figure 13B**). On aluminum substrate in particular, the bond strength was exceptional for the Diels-Alder formula. These results demonstrate the versatile adhesion performance of the Diels-Alder based networks using different substrates and surface chemistry.

2.6 Cured mechanical properties

The mechanical properties of thermally reversible DA-1 and DA-4 were compared to the moisture cured PUR benchmark. As a result of higher crosslink density obtained from low molecular weight prepolymers, DA-1 exhibits the highest break stress and lowest elongation (**Table 2**). Due to the higher molecular weight backbones used in M-2 and M-3 prepolymers, DA-4 has a lower crosslink density. This results in stress-strain and elongation properties similar to PUR benchmark.

Figure 13.

(A) Lap shear strength comparison of DA-1, DA-4 and control PUR at ambient temperature and 80°C using Beechwood substrate. (B) Bond strength comparison of DA-4 and control PUR using different substrates at ambient temperature. Reproduced from [17] with permission from Royal Society of Chemistry.

Formula	Modulus ^a	Break Stress ^a (MPa)	Elongation at break ^a (%)	Creep failure temperature ^b (°C)
DA-1	70	10.5	140	90
DA-4	124	7.7	480	80
Control PUR	93	5.4	735	>110

^aDetermined by tensiometric analysis (100 N load cell, 100 mm.min⁻¹).

^bDetermined by vertical creep measurements (25 × 25 mm bond overlap, 1 Kg static load).

Table 2.

Mechanical properties of films and creep resistance measurements for DA-1 and DA-4 compared to PUR control.

It should be noted that DA-4 and the reference PUR both comprise semi-crystalline polyester segments at a similar overall concentration.

The mechanical properties of DA-1, DA-2 and DA-4 Diels-Alder networks were evaluated by DMTA using 250 μm cured films (**Figure 14**). The 3 networks have high stiffness below their respective T_g . DA-4 has the highest mechanical properties due to the presence of the semi-crystalline segments resulting from M-2 and the modulus changes significantly above ambient temperature as a consequence of melting (**Figure 14A**). Above the T_g and T_m (for DA-4), the change in modulus is slow for the 3 networks in the temperature range 40–80°C. There is then rapid

Figure 14.

(A) Storage modulus vs. temperature of DA-1, DA-2 and DA-4. (B) Tanδ vs. temperature of DA-1, DA-2 and DA-4 from DMTA on 250 μm films. Reproduced from [17] with permission from Royal Society of Chemistry.

decrease in modulus at higher temperature (above 80°C) with the $\tan \delta$ reaching 1 (**Figure 14B**), at which point there is a transition from a solid to a liquid phase. This is the temperature range where the Diels-Alder equilibrium shifts predominately to the prepolymeric dissociated state resulting in stretching and failure of the film samples being tested.

Comparison of crosslink densities of the Diels-Alder networks shows a correlation between crosslink density and the rapid decrease in storage modulus (G') above 80°C. DA-1 has a higher functional group concentration because of lower molecular weight reactants (1.63 mol.Kg⁻¹, calculated based on stoichiometry of reagents), which results in higher crosslink density. Even though the Diels-Alder equilibrium starts to shift to the prepolymeric state above 80°C, the higher crosslink density present in DA-1 delays the rapid decrease in G' to approximately 97°C. In contrast, DA-4 comprising a lower crosslink density (lower functional group concentration of 0.39 mol.Kg⁻¹) shows a rapid change in modulus at approximately 85°C.

A further important property of RHM adhesives is their creep behavior at higher temperature under static load. The creep resistance of reversible DA-1 and DA-4 was compared with the irreversible moisture cure PUR control up to 110°C (**Table 2**). This upper temperature limit was chosen based on $\tan \delta$ data, which shows liquid-like behavior for DA-1 & DA-4 networks (**Figure 14**). Creep experiments were performed on bonded joints under a static load of 1 Kg in an oven held at a particular temperature for 24 h. The creep resistance of the reversible Diels-Alder system correlates well with the crosslink density of the cured network. The DA-1 system with a higher crosslink density was resistant to creep at 80°C but the joints failed at 90°C. The DA-4 system which has a lower crosslink density failed at 80°C but was resilient to creep at 70°C. The irreversible PUR control was creep resistant over the entire temperature range. Both the Diels-Alder networks were creep resistant in a temperature range well above their T_g and T_m (for DA-4). This result indicates a significant advantage of these reversible Diels-Alder based networks as compared to some of the reported creep behavior of other covalently adaptable networks [20]. The failure temperature observed in the creep experiment of DA-1 and DA-4 networks correlates well with their respective DMTA data, which indicates significant change in stiffness close to the failure temperature (**Figure 14**). Since the data shows strong dependency of creep resistance on crosslink density, it is feasible to develop new Diels-Alder systems with improved performance by changing the architecture of the furan and maleimide components.

2.7 Reversibility and recyclability

For a truly sustainable adhesive, its material properties and adhesion should not change significantly after multiple reprocessing and re-use cycles. In several industrial applications (including assembly of components in the automotive industry) the bonded substrates need to be repositioned if a defect is found or recycled at the end of their life. This requires that the adhesive shows similar performance when subjected to multiple bond, de-bond, re-bond cycles. The repeatability of lap shear adhesion of DA-1 and DA-4 formulas over multiple cycles was tested using adhesive films cured between aluminum joints. Initial bonds were formed using a film adhesive that was heated to the hotmelt dissociated state to wet the substrates and then cured for 7 days at ambient temperature before bond strength measurement. For the 2nd, 3rd and 4th re-use, the same joints were broken after the lap shear test and reassembled using the residual adhesive on the surface by heating and re-bonding of the broken joints. The adhesion data over multiple cycles is shown in **Figure 15**. Both DA-1 and DA-4 are relatively robust in performance after multiple bond, de-bond,

Figure 15.

Bond strengths of DA-1 and DA-4 over several cycles of bonding, de-bonding and re-bonding using the same aluminum substrate. Reproduced from [17] with permission from Royal Society of Chemistry.

re-bond cycles. The bond strength of the DA-1 system is unchanged after 4 re-use cycles while DA-4 shows a small decrease in strength (**Figure 15**). This is a significant result despite the likelihood that some adhesive could be lost or migrate out of the bond line during multiple heating, re-bonding and lap shear testing.

2.8 Development of the concept to soft cured Diels-Alder networks

As an extension of the RHM study, an initial investigation was performed on Diels-Alder based systems that give cured networks with a lower modulus at ambient temperature, approaching the pressure sensitive adhesive (PSA) region (10^4 to 10^5 Pa). This study required the synthesis of higher molecular weight maleimide prepolymer M-5 comprising an amorphous polyester segment with a lower T_g . To this end, M-5, containing Dynacol 7250 backbone (molecular weight 5500 g. mol⁻¹ and T_g – 50°C as compared to 3500 g. mol⁻¹ and T_g – 30°C for Dynacol 7231 used previously), was made using a process similar to that used for M-3 synthesis (**Figure 16**) [18]. An additional furan F-7 possessing a very soft backbone was also made by simple addition of furfuryl alcohol to Desmodur XP2599 (Covestro). The structure of this commercially available isocyanate (functionality >3) is not known and the stoichiometry for the synthesis of F-7 was calculated based on isocyanate equivalent weight.

M-5, when polyester is Dynacol 7250

F-7 (polyfunctional furan derived from Desmodur XP2599)

Figure 16.

Prepolymers used for the development of soft Diels-Alder cured networks.

Formula	F-2	F-7	M-5	Modulus (Pa) ^a	Elongation at break (%) ^a
DA-9	8		92	6.2×10^5	658
DA-10		20.2	79.8	5.1×10^5	579

^aDetermined by tensiometric analysis (100 N load cell, 100 mm.min⁻¹).

Table 3.
Diels-Alder formulas used for the development of soft cured networks. The formulation components shown are in weight %.

Figure 17.
Melt viscosity stability of DA-9 and DA-10 formulas as a function of time at 135°C.

The cured network DA-9 comprising F-2 and M-5 showed high elongation and a low modulus. DA-10 comprising F-7 and M-5 showed even lower modulus and similar elongation properties (**Table 3**). **Figure 17** shows that melt viscosity remains relatively low for these types of formulation and that thermal stability is good over several hours at 135°C. While these amorphous networks with relatively low crosslink density are not expected to have the same level of creep resistance as the networks DA-1 and DA-4 required for RHM applications, they may be sufficient for PSAs. In conventional solvent borne PSA technology, permanent crosslinking is typically achieved by the use of low level of metal chelates, which upon evaporation of the solvent bind with pendant hydroxyl or carboxylic functionality from the polymer backbone and provide crosslinks [21]. The degree of crosslinking is controlled by the amount of metal chelate used in the formulations. The crosslinking mediated by the Diels-Alder reaction could potentially be an effective metal-free substitute for new PSA development especially as a hotmelt PSA. In hotmelt PSA's, the adhesive is applied from the melt to substrates (no solvent used unlike solvent borne PSA and environmentally friendly) and the adhesive after application to substrates requires a crosslinking mechanism (such as UV induced crosslinking) for sufficient shear adhesion strength. Since the depolymerization gives the melt state (and sufficiently low viscosity to wet the substrates), the Diels-Alder mediated room temperature crosslinking could be an effective alternative method to achieve crosslinking in hotmelt PSAs. More formulation work (for example with tackifiers) is needed to develop formulations that would meet the tack, peel and shear adhesion requirements.

3. Conclusions

Polyester and polyurethane functional furans were reversibly copolymerized in the bulk with multifunctional maleimide prepolymers in a successful demonstration of a thermally reversible reactive hotmelt (RHM) adhesive concept that is

isocyanate-free. At the hotmelt temperature, the adhesive remained in the pre-polymeric dissociated state with a low melt viscosity, enabling facile application to substrates and bond formation. Upon cooling, ambient temperature cure took place mediated by the Diels-Alder cycloaddition reaction. The reversible Diels-Alder RHM adhesive showed good thermal stability at the hotmelt application temperature. The green strength obtained after immediate cooling was highly tunable by choice of the prepolymers used in the formulation. The cure rate observed with the reversible RHM adhesive was similar to the moisture cure PUR benchmark and the new RHM adhesive showed versatile adhesion on a range of substrates. Mechanical and tensile properties were tunable depending on the choice of backbone present on the prepolymers used. A strong correlation between crosslink density and creep performance was observed. Repeated bonding, de-bonding and re-bonding experiments demonstrated a similar level of performance over multiple cycles. The adhesive reversibility would enable recycling or repositioning of bonded components several times without significant deterioration in performance. Diels-Alder networks with lower crosslink density have also been developed, which could be adapted for hotmelt pressure sensitive adhesive applications. Several polyfunctional furans and maleimide prepolymers were synthesized in multi-Kg scale to demonstrate industrial scalability.

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Conflict of interest

The authors declare no conflicts of interest.

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